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TITLE: DEVELOPMENT OF A RAPID RADIOCHEMICAL PROCEDURE FOR THE
SEPARATION OF URANIUM-235m FROM PLUTONIUM-239

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Development of a Rapid Radiochemical Procedure for the Separation of $^{235\text{m}}\text{U}$ from ^{239}Pu

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ABSTRACT

We have developed a rapid radiochemical procedure for the isolation and purification of $^{235\text{m}}\text{U}$ ($t_{1/2} = 26$ minutes) from ^{239}Pu samples up to 250 mg. The purpose of developing the procedure was to measure the thermal neutron fission cross section of the isomeric meta state of ^{235}U .

We used rapid small scale anion exchange columns that absorbed uranium in concentrated HBr but did not absorb plutonium. Uranium was easily eluted with very dilute HF . The separation time required 25 to 35 minutes. We were able to attain a separation factor of uranium from plutonium of approximately 1×10^{10} with samples ranging from 1×10^{10} to 3×10^{11} . The ratio of the fission cross sections for the meta to ground state was measured to be 1.42.

INTRODUCTION

This work described here is a part of a larger experiment where the measurement of the ratio of the thermal neutron fission cross section of 26-minute ^{235}U meta to that of the ^{235}U ground state is reported (1). Cross section measurements for excited states of nuclei are somewhat lacking and represent important information in our understanding of nuclei structure. Consequently, experimental measurements of this type on $^{235\text{m}}\text{U}$ are of interest in providing information related to astrophysical phenomena and assisting theoretical modeling for excited states.

In 1957 the discovery and nuclear characterization of $^{235\text{m}}\text{U}$ (2,3) was reported, indicating the half-life of this isomer to be 26.05 ± 0.11 minutes and having a $1/2+$ energy level at 73 ± 5 kev above ground level. The production rate is 99.96% from the alpha decay ^{239}Pu ($t_{1/2} = 24,110$ years). In these studies as others that were to follow, the $^{235\text{m}}\text{U}$ was detected by measuring the conversion electrons. Following its discovery, sev-

eral interesting studies were reported that revealed the chemical effects on the observed half-life of this isomer (4-6). Samples were collected from the alpha recoil in the decay process. The method showed promise in scaling up the number of collected $^{235\text{m}}\text{U}$ from larger surface areas of plutonium. This principle was utilized in the measurement of the fission cross sections from a Russian study, where the recoiled $^{235\text{m}}\text{U}$ was collected onto a metal collection plate from a 1 m^2 area of plutonium (7).

Some of the first attempts in our laboratory utilized the principles of recoil collection of the $^{235\text{m}}\text{U}$ atoms. However, using a plutonium surface area of 0.1 m^2 , the attempts did not prove successful. Thus, using the radiochemical expertise in the separation of the actinide elements, the development of a rapid radiochemical technique was initiated.

It was envisioned to have a plutonium source (cow), devise a scheme to separate uranium from this cow, purify the uranium by removing the maximum amount of plutonium, complete the mounting, and start irradiating in a thermal neutron flux and counting (in a fission chamber) within a fixed short time period.

EXPERIMENTAL DEVELOPMENT

The procedure that was initially developed used the principles of the separation of uranium from plutonium on an anion exchange column from concentrated HBr medium. Plutonium is not absorbed but uranium is. With successive washings of concentrated HBr and with the elution of uranium from the column with very dilute HF, a cycle of purification could be established and repeated. The following is a description of that procedure. A more detailed procedure is described later which shows the final procedure in flow diagram detail.

Plutonium-239 (approximately 70 mg) was dissolved in 48% HBr and passed sequentially through three separate anion exchange columns to remove the uranium that had grown in since the previous experiment. The time of the final step of this operation was marked as the beginning of the ingrowth period for $^{235\text{m}}\text{U}$, a period of about 15 min.

utes. The newly grown-in ^{235}mU was then absorbed onto a new anion exchange column and was washed three times with concentrated HBr to remove traces of plutonium. The uranium was eluted with a very dilute HF solution. Enough 48% HBr was added to the collected uranium solution to make the solution approximately 20-30% HBr, a concentration that was thought to prevent the adsorption of plutonium and maximize the absorption of uranium on the next column cycle. We repeated the absorption, wash, and removal of uranium from another anion exchange column. The eluant was then evaporated to a small volume, cooled, and the anion exchange cycle was repeated. The final eluant was then again evaporated to a small volume, deposited onto a platinum disc, flamed and mounted in the fission chamber for irradiation and simultaneous counting of fissions.

The fission chamber was developed and constructed in our laboratory. The details of the chamber are described in our report (1). The background for the system in a thermal neutron flux of 5×10^{11} n/sec/cm² was about 6 counts per second.

The separations were performed at the Los Alamos Omega West Reactor site in the radiochemistry laboratory. A portable plastic glove box was fitted into the hood and all manipulations for the initial separation-purification were conducted within it.

The time required for this separation was usually 30-40 minutes. We were able to attain a separation factor of uranium from plutonium of about 1×10^{10} . To estimate the uranium contamination that could arise in the chemical process, we determined mass spectrometrically that all the reagents used in the process had a uranium level lower than 5×10^7 atoms for the volumes typically used for the separation.

This procedure requires the use of ultra-pure reagents, including type-1 water and all new glassware for each separation. Consequently all equipment used in these experiments was new and had been rigorously cleaned with 4 M HNO₃, rinsed with Milli-Q water, dried, and stored in sealed plastic containers. High quality reagents such as Merck Suprapure HBr and ultra pure Seastar HF were used in the preparation of the reagents. Columns for the separation were prepared in blue Eppendorpf plastic pipette tips that were plugged

with rigorously washed quartz fiber. Actual column preparation took place in a class-100 clean room. Pretreated AG MP1 50-100 mesh resin was used for the anion exchange resin. It has a rapid flow rate. All columns were preequilibrated with concentrated HBr before use. Flow rates could be increased by gently applying a pressure onto the top of the column with a syringe fitted with a rubber stopper. The platinum discs were new and were individually checked for fissionable materials by irradiating them in the fission chamber prior to use.

There were three possibilities of observation of the fission rate as a function of time once the sample had been prepared and irradiated. If the thermal neutron cross section for the meta state (σ_m) is greater than that of the ground state (σ_g), we would anticipate a decrease in the fission rate as a function of time (see figure 1). Likewise, if $\sigma_g > \sigma_m$, then there would be an apparent increase or growth in the fission rate as the meta state atoms were being converted to the ground state atoms that have a larger cross section. The final possibility is that $\sigma_g = \sigma_m$ and no change in the fission rate would be observed.

The general expression used to calculate the ratio of the isomeric-to-ground state cross section ratio, $R = \sigma_m/\sigma_g$, is given as follows:

$$R - 1 = b / \{ [(1 - e^{-\lambda})/\lambda] [(1 - e^{-\lambda t})/\lambda t] (a - B - "Pu") \}$$

where a and b are constant coefficients for the function, λ is the decay constant for ^{235m}U , t is the time lapsed from the end of the ingrowth period to the count time. The count interval is 1 minute, B is the fission background of the Pt disc and "Pu" is the plutonium fission rate contribution arising from any Pu in the final sample as determined by a spectrometry of the disc.

Over a period of approximately one year we observed R values < 1 indicating that the ground state cross section was greater than the meta state. Results were scattered and lead to some questions.

Complications due to the low plutonium concentration of the cow, electronic/counting failures, and a suspicion of other sources of uranium in the samples either from outside sources or from sources or causes of the analysis were considered. We then begin a systematic review of the chemistry system where we investigated several possibilities of the excess amount of uranium in the final sample. The fission rates were higher than could be accounted for from the simple chemical separation of the sample if all the uranium had been removed.

First, we investigated the reagent-procedure aspect of the separation. We then conducted several separations under conditions of a class-100 clean room and we found that the samples that we delivered to the reactor contained about 8×10^8 atoms of ^{235}U , an amount that would not cause an appreciable concern for the determination. We then turned our attention to the possibility of environmental uranium contamination at the place where we actually did the analysis, the Los Alamos Omega West Reactor. Under exact operational conditions, we ran blank samples that were irradiated. The results were the same as the class-100 clean room experiments. Our conclusion then was that no significant amount of uranium was being introduced into the sample from the reagents, glassware, supplies or handling and the environment of the laboratory did not make any contribution.

Finally, we suspected that there was an incomplete clean up of the ^{235}U that had grown in from the ^{239}Pu cow overnight or the previous experiment. The following experiments were planned and conducted using ^{233}U (α emitter) and ^{239}U (β/γ emitter). Using conditions that were identical to that of the actual separation we loaded the tracer onto the anion column in varying concentrations of HBr (concentrated to about 4.5 M). This was in a volume of approximately 5 mL. The column was then washed 3 times with 3 mL concentrated HBr and the uranium was finally stripped with 1.2 mL 0.006 N HF . The results are shown in figure 2. It became very clear that our conditions for loading, washing and stripping the uranium were not 100%. We also found that a small percent of the initial uranium tracer (^{239}U in this case) remained on the column. Therefore, we

concluded that the initial loading of the solution was where the problem occurred. Built up uranium in the plutonium cow was not being removed by the three column clean up cycle. In an earlier report (8) it is indicated that absorption of uranium under these conditions was nearly 100% onto the column. But it became apparent that conditions of that study (8) allowed the aqueous and resin phases to come to equilibrium over an extended period of time which was not the case in our separation scheme. Thus, we felt that the results of our study were not inconsistent with that which had been previously reported in light of the equilibrium condition variability.

With the information gained from these exercises the radiochemical procedure was modified to accommodate these observations. Figure 3 provides the flow diagram for the separation. Basically, the only differences in the procedure are the 5-column clean up before allowing the ingrowth period to be started and the elimination of the evaporation step in the procedure before loading onto the final column (which was too time consuming). Furthermore, we incorporated numerous other precautions in the actual manipulations. Rubber gloves were changed after every contact with the plutonium solution. Reagent bottles were changed after every step. Column tips were carefully washed with appropriate solvents to eliminate lingering drops that could contain plutonium. Rubber stoppers and syringes were changed out after each use. Columns were placed at various positions on the column rack depending upon the step in the separation. Also, after each run, the glove box was completely scrubbed down and checked for alpha activity before the next use. The final steps of the separation and mounting were conducted in an area where no plutonium had been exposed. By enforcing all these restrictions, we were able to conduct the separations within the time period required and were able to deliver samples that contained very little or no plutonium with expected amounts of fission rates for the samples being used.

RESULTS AND DISCUSSION

The results of the measurements for R are given in Table I. The amount of Pu detected

in these samples is also listed. This represents a decontamination of approximately of 1×10^{12} of uranium from plutonium. We were able to deliver between 6×10^{10} and 3×10^{11} atoms $^{235\text{m}}\text{U}$ in this series.

Figure 4 is given to illustrate a typical run for this suite of experiments. A dotted line indicates what the curve would look like if a value of $R = 2.2$ were observed. This is the value that was reported by the Russian work (4) and clearly shows that our measurements can distinguish between the two values quite easily.

While conducting these experiments we learned of other measurements not yet published where $R = 1.61 \pm 0.44$ for 5 meV most probable neutron energy and $R = 2.47 \pm 0.45$ for 70-meV most probable neutron energy (9). Our value (1) is 1.42 ± 0.04 for 75.5-meV most probable neutron energy. The Russian value (7), $R = 2.2$, did not have a neutron energy assigned to it. The agreement is not good for the four values, but these may give some indication of resonance absorption peak.

All the recoil collection techniques used to make other measurements suffer from Pu contamination in the final samples and also from low $^{235\text{m}}\text{U}$ atom concentrations. Hence large errors are observed. As a matter of comparison we find that the radiochemical procedure, although more tedious and demanding, is able to provide clean samples and a large number of $^{235\text{m}}\text{U}$ atoms.

We have successfully developed and employed a rapid radiochemical procedure for the separation and purification of $^{235\text{m}}\text{U}$ from ^{239}Pu (in the 200 mg range) in a time period of approximately 35 minutes. In doing so we have measured the ratio of meta-to-ground neutron fission for ^{235}U with good statistics. Plans for modifying the scheme to accommodate larger plutonium sources to produce more $^{235\text{m}}\text{U}$ atoms being irradiated in lower neutron fluxes at other energies is being considered.

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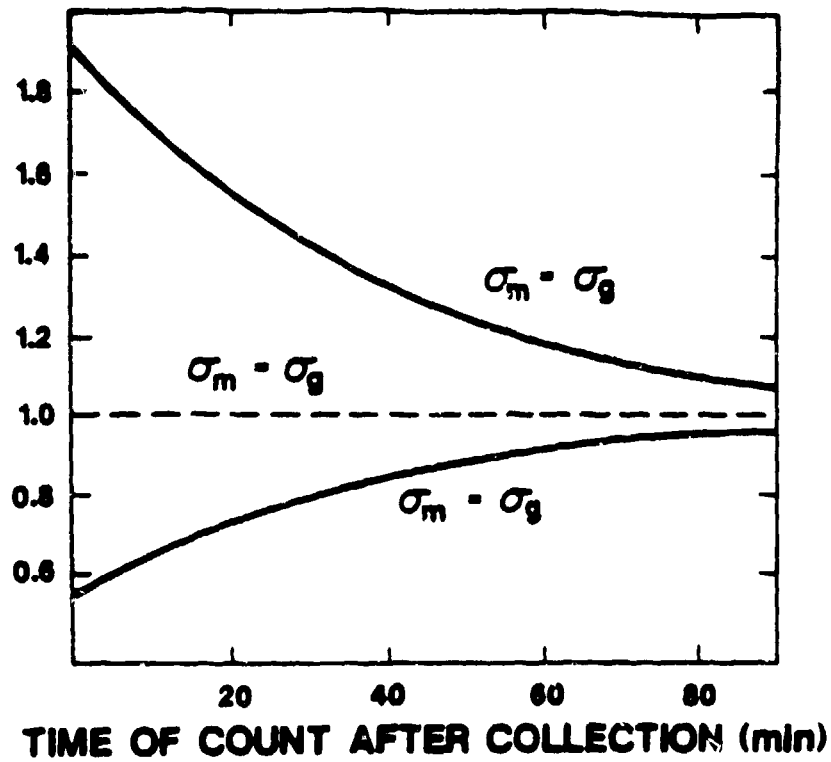


Figure 1. Anticipated fission activity trends of separated ^{235}U in thermal neutron flux.

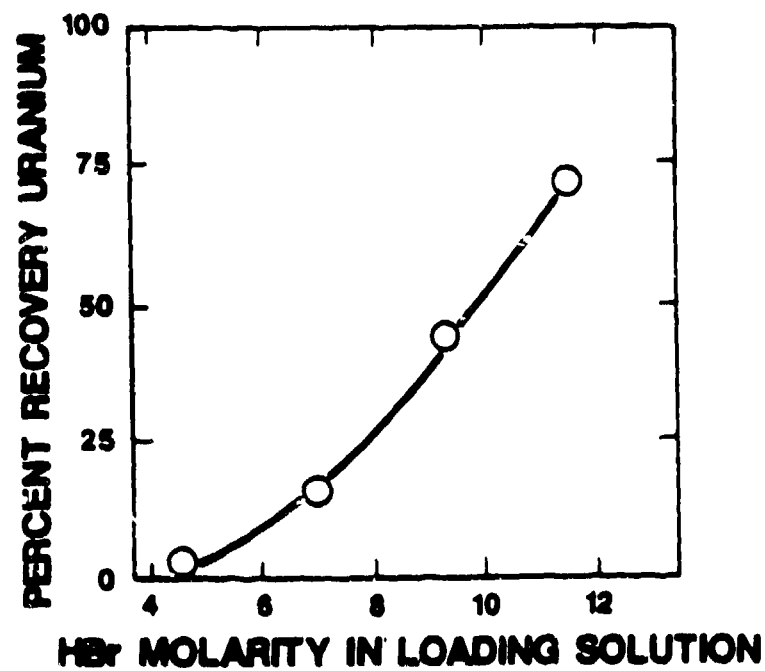


Figure 2. Recovery of tracer uranium from AG-MPl anion column from HBr solutions under separation conditions.

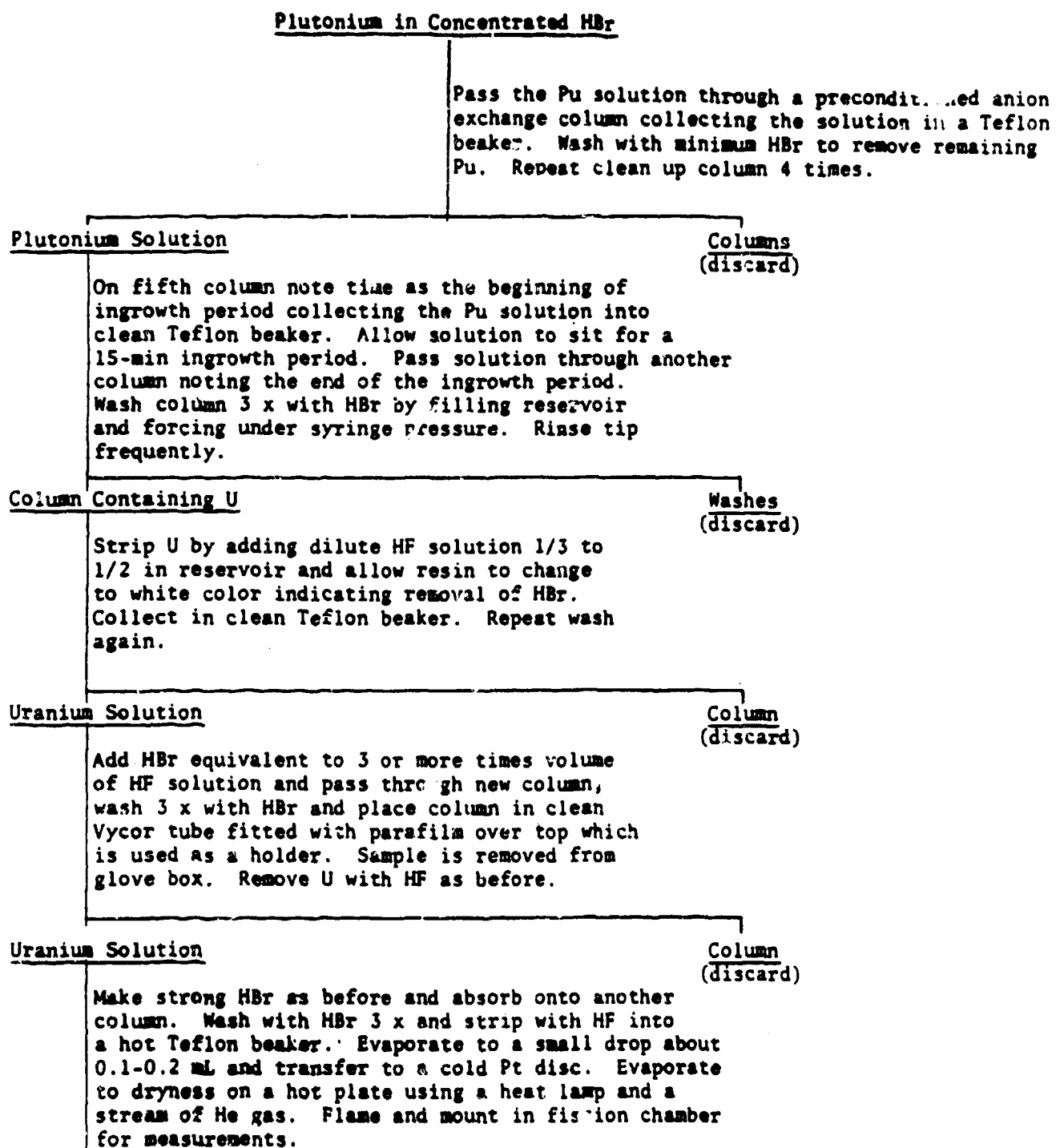


Figure 3. Flow diagram for the rapid radiochemical separation of uranium from milligram quantities of plutonium.

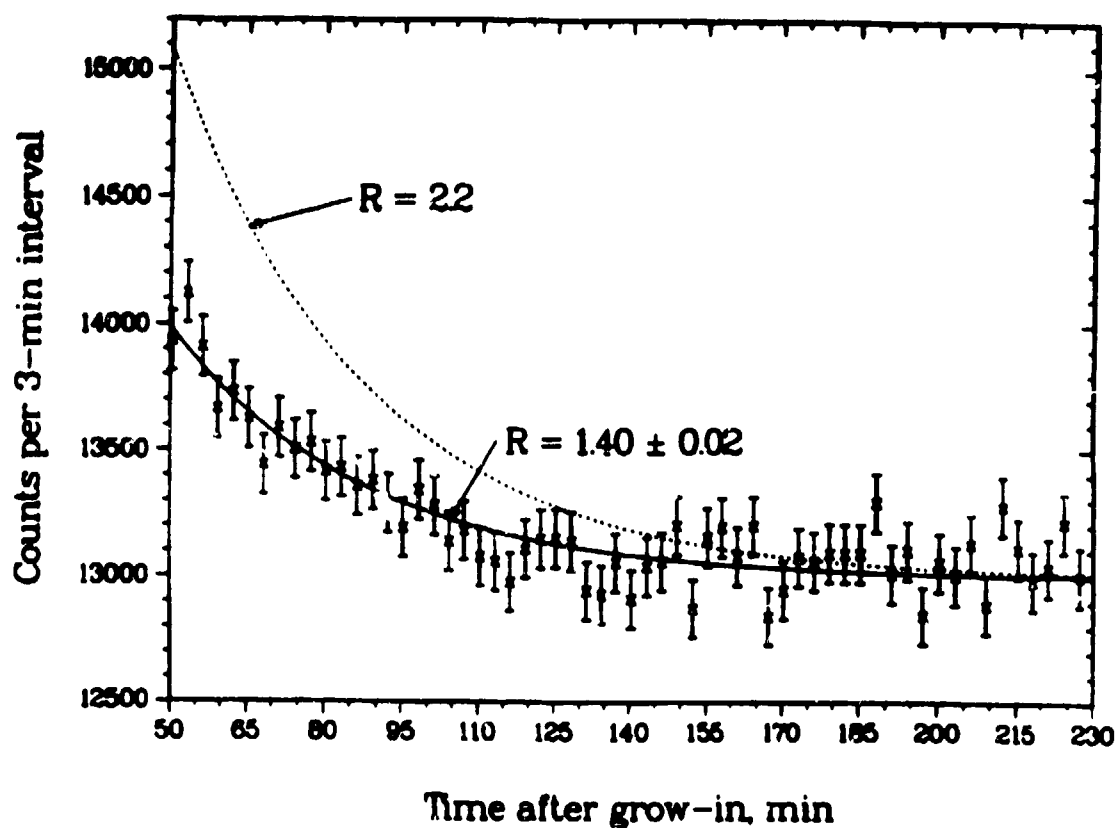


Figure 4. Fission rate of separated $^{235}\text{U}^{\text{m}}$ (flux normalized).

Table I. Results of the Meta-to-Ground State Thermal Neutron Cross Section Measurements for ^{235}U .

Atoms ^{235}U	Atoms ^{239}Pu Contaminant	$R (\sigma_{\text{m}}/\sigma_{\text{g}})$
6.39×10^{10}	5.56×10^8	1.419 ± 0.064
3.68×10^{11}	4.32×10^8	1.403 ± 0.022
1.78×10^{11}	$< 1 \times 10^8$ *	1.437 ± 0.022
1.02×10^{11}	$< 1 \times 10^8$ *	1.374 ± 0.037
6.69×10^{10}	1.02×10^8	1.466 ± 0.011
1.76×10^{11}	$< 1 \times 10^8$ *	1.478 ± 0.022
8.06×10^{10}	6.21×10^8	1.392 ± 0.032
1.35×10^{11}	$< 1 \times 10^8$ *	1.386 ± 0.022
Average		$1.42 \pm 0.04^{**}$

*Below detection limits.

**Weighted average of individual measurements.